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**GB 1435524**

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(54) **Composition for Production of Cold Drawn Film**

(57) A polymer composition useful for production of a stretched, shrinkable wrapping film by cold-drawing comprises a homogeneous blend of:

(b) an ethylene- $\alpha$ -olefin copolymer

elastomer having a density of not more than  $0.91 \text{ g/cm}^3$  and

(c) at least one polymer selected from crystalline polypropylene and crystalline polybutene-1, the amounts of the components being such as to satisfy in terms of weight ratio the expression  $0.90 \geq b/(b+c) \geq 0.30$ .

## SPECIFICATION

## Composition for Production of Cold Drawn Film

In our copending patent application no.

- 5 39283/78 we describe and claim a cold drawn film having a tensile strength of not less than 5.0 kg/mm<sup>2</sup> and a haze of not more than 4.0%, which film comprises a homogeneous blend of components (A), (B) and (C) in the combinations (A)+(B), (B)+(C) or (A)+(B)+(C), wherein (A) is at least one polymer selected from low-density polyethylene and copolymers of ethylene with vinyl ester monomers, unsaturated aliphatic monocarboxylic acids and alkyl esters of said carboxylic acids which are all copolymerizable with ethylene,

(B) is an ethylene- $\alpha$ -olefin copolymer elastomer having a density of not more than 0.91 g/cm<sup>3</sup>, and

- 20 (C) is at least one polymer selected from crystalline polypropylene, high-density polyethylene or crystalline polybutene-1.

The said copending application also describes and claims a method for producing the above cold drawn film. The present invention provides certain compositions which may be used to produce the film which is the subject of patent application no. 39283/78.

- 30 The present invention provides a composition comprising a homogeneous blend of components (b) and (c); wherein

(b) is an ethylene- $\alpha$ -olefin copolymer elastomer having a density of not more than 0.91 g/cm<sup>3</sup> and

- 35 (c) is at least one polymer selected from crystalline polypropylene and crystalline polybutene-1,

the amounts of the components being such as to satisfy in terms of weight ratio the expression

- 40  $0.90 \geq b/(b+c) \geq 0.30$ .

The manufacture of a cold drawn film from this composition is described in detail in patent application no. 39283/78.

- 45 The thermoplastic elastomer comprising a copolymer of ethylene with at least one  $\alpha$ -olefin as the component (b) is a non-rigid copolymer of ethylene with at least one  $\alpha$ -olefin selected from  $\alpha$ -olefins having from 3 to 12 carbon atoms. As occasion demands, this elastomer may be further

- 50 copolymerized with a small amount of a hydrocarbon of the polyene structure such as, for example, 1,4-hexadiene, ethylidene norbornene, etc. Examples of the  $\alpha$ -olefin suitable for this purpose include propylene, butene-1, hexene-1,

- 55 heptene-1, 4-methyl-1-pentene, octene-1, etc. Of these  $\alpha$ -olefins, preferable are propylene and butene-1. In any of these copolymers, the ethylene content is desired to fall in the range of from 20 to 90 mol %, more desirably from 40 to 90 mol %, preferably from 65 to 88 mol %.

60 These copolymers are of such nature that the density is not more than 0.91 g/cm<sup>3</sup>, the Vicat softening point as determined in accordance with ASTM D-1525 (value under 1 kg of load) is not

- 65 more than 80°C, preferably not more than 70°C and the crystallinity in the rubbery zone generally ranges from substantial amorphousness to low partial crystallinity of the order of not more than 30% of crystallinity degree determined with X-ray.

- 70 The component (b) is particularly desired to be a copolymer of ethylene with propylene or butene-1, and this copolymer may, when necessary, incorporate therein a small amount of a compound of the diene structure in the form of a copolymer. It is, therefore, a thermoplastic elastomer in the form of a random copolymer obtained by the polymerization using a catalyst of the system produced with a vanadium compound and an organic aluminum compound. The elastomer possesses a melt index of from 0.1 to 10, preferably from 0.2 to 6.

- 85 The polymer (c) is at least one selected from crystalline PP (polypropylene) and high molecular PB-1 (polybutene-1) which each possess relatively high rigidity and relatively high degree of crystallinity. The polymer has relatively high rigidity and desirably a Vicat softening point of not less than 100°C.

- 90 The crystalline PP which is one of the members of the group from which the component (c) of the composition of this invention is selected is a crystalline PP with high isotacticity usually available on the market. It is desired to be a homopolymer of propylene or any of the copolymers of propylene with not more than 10 mol % of ethylene, 1-butene or some other  $\alpha$ -olefin. It may be a mixture of these copolymers.

- 100 The polybutene-1 is desired to be a crystalline homopolymer of more than 90 mol % of butene-1 with other monomer. Unlike a liquid-to-waxy low molecular polymer, these polymers are desired to possess a melt index in the range of from 0.2 to 10 for the same reason as mentioned above. Of the possible members of the aforementioned group, it is desirable to use chiefly the crystalline polypropylene.

- 110 The composition of the present invention comprises a combination of components (b)+(c). The mixing ratio of these components in terms of weight ratio is such as to satisfy

$$0.30 \leq c/(b+c) \leq 0.90$$

and more desirably to satisfy:

$$0.40 \leq c/(b+c) \leq 0.87$$

- 115 and preferably to satisfy:

$$0.50 \leq c/(b+c) \leq 0.85$$

- 120 If the amount of the non-rigid component (b) is less than the allowable lower limit indicated above, the blend fails to manifest the expected synergistic effect and, therefore, suffers from inferior processibility, lowered film strength and impaired optical properties and low-temperature shrinkability. If the amount is more than the

allowable upper limit, a tubular sheet produced from the blend is degraded in film-forming property and stretchability and becomes so soft as to entail the phenomenon of film-to-film

- 5 blocking and the produced film exhibits insufficient heat resistance, sealability, strength and optical properties. The component (c) serves to improve not only modulus but also seal properties such as, for example, thermal
- 10 properties including heat resistance particularly in the higher portion of the allowable temperature range.

- As described above, this invention permits the quenched tubular sheet which has been produced from the composition obtained by using the specific components in their respective specific amounts to be cold stretched with ample stability in the manner to be described hereinafter. If the tubular sheet is further treated with a specific high-energy ray so as to have the gel content (insolubles in boiling xylene) or the melt index brought into a specific range, the components in the composition produce a synergistic effect such as to manifest the desired cold stretchability (at temperatures in the range of from 20 to 100°C) under specific stretching conditions, giving rise to a film of outstanding properties.

- Now, the composition produced by using the components in the preferred mixing ratio will be described. Generally, the crystalline PP component (c) is hardly crosslinked even when it is subjected to treatment with high-energy radiation. The elastomer of the copolymer of  $\alpha$ -olefin (b) exhibits rather high compatibility with polypropylene and induces the reaction of crosslinking readily. Consequently, the synergistic effect brought about from the proper dispersion of the components in the composition is coupled with the synergistic effect which issues from the action of the high-energy radiation. The combination of these synergistic effects is believed to result in the production of a film wherein there is formed a specific, molecularly heterogeneous crosslinked matrix. The treatment with high-energy radiation, accordingly, improves notably the stable cold stretchability of the tubular sheet and the film's heat resistance and heat seal strength, enhances the thermal shrinkability and strength of the film at low temperatures, represses possible degradation in optical properties and physical properties after thermal shrinkage (such as optical properties, seal strength and mechanical strength) and expands the range of packaging temperatures. Thus, the properties possessed by the film which is produced from the crosslinked tubular sheet far excel those possessed by the plasticized PVC film and PP film which have heretofore been rated to be the best films.

- 60 The composition of this invention may also be effectively used when it is mixed with some other composition insofar as the amount of the additive composition does not impair the stretchability and various other properties of a film which is
- 65 produced from the composition.

The compositions of this invention are illustrated in the following Examples.

#### Example 1

- 80 parts by weight of an ethylene- $\alpha$ -olefin copolymer elastomer (melt index: 0.25, Vicat softening point: less than 50°C, density 0.88 g/cm<sup>3</sup>,  $\alpha$ -olefin: butene-1,  $\alpha$ -olefin unit content 20 mol %) were mixed with 20 parts by weight of crystalline polypropylene (melt index: 0.8, ethylene unit content: 6% by weight). The composition was extruded, at the maximum temperature of the cylinder part of 250°C, from an annular die 150 mm in diameter having a slit of 1.5 mm provided with a mixing head type screw 65 mm in diameter and a ratio (L/D) of 37. The extruded film was quenched with water about 10 cm from the lip of the die. A raw tubular film 200  $\mu$  in thickness and with a deviation in thickness of  $\pm 2.0\%$  was obtained.
- 85 The production of a stretched film is described in Example 4 (Run No. 22) of GB 2007685.

#### Example 2

- 80 parts by weight of ethylene- $\alpha$ -olefin copolymer elastomer ( $\alpha$ -olefin: propylene,  $\alpha$ -olefin unit content: 20 mol %, melt index: 0.25, density: 0.88 g/cm<sup>3</sup>, Vicat softening point: less than 40°C) were mixed with 20 parts by weight of crystalline polypropylene (ethylene unit content: 5% by weight, melt index: 0.6, Vicat softening point: 120°C, density: 0.87 g/cm<sup>3</sup>). The composition was plasticized and kneaded, at the maximum temperature of the cylinder part of 260°C, by a mixing head type screw 45 mm in diameter (L/D=44), and pelletized. The composition was extruded through an extruded 45 mm in diameter (L/D=37) fitted with a T-type die which had a slit 1 mm in thickness and 40 cm in width. While extruding a liquid additive was injected into the rear part of the cylinder under pressure. The melted polymer composition extruded from the die was introduced into water to form a raw tubular film 100  $\mu$  in thickness. The production of a stretched film is described in Example 10 (Run No. 29) of GB 2007685.

#### 110 Claims

1. A composition comprising a homogeneous blend of components (b)+(c); wherein (b) is an ethylene- $\alpha$ -olefin copolymer elastomer having a density of not more than 0.91 g/cm<sup>3</sup> and (c) is at least one polymer selected from crystalline polypropylene and crystalline polybutene-1, the amounts of the components being such as to satisfy in terms of weight ratio the expression

$$0.90 \geq b/(b+c) \geq 0.30$$

2. A composition according to Claim 1, wherein the ethylene- $\alpha$ -olefin copolymer as the component (b) has an ethylene unit content of not more than 90 mol % and not less than 20 mol %.

3. A composition according to Claim 1, wherein the ethylene- $\alpha$ -olefin copolymer as the component (b) has an ethylene unit content of not more than 90 mol % and not less than 40 mol %.
- 5 4. A composition according to any one of Claims 1 to 3, wherein the elastomer as the component (b) is a non-rigid copolymer having a Vicat softening point of not more than 80°C and a degree of crystallization of not more than 30%,
- 10 wherein the  $\alpha$ -olefin component contained therein is at least one  $\alpha$ -olefin having from 3 to 12 carbon atoms.
- 15 5. A composition according to any one of Claims 1 to 4, wherein the elastomer as the component (b) is a random copolymer wherein the  $\alpha$ -olefin component is propylene or butene-1.
- 20 6. A composition according to any one of Claims 1 to 5, wherein the ethylene- $\alpha$ -olefin copolymer as the component (b) has copolymerized polyene units in addition to the main components derived from ethylene and  $\alpha$ -olefin.
7. A composition according to Claim 6, wherein the polyene contains not more than 5
- 25 mol % of a non-conjugate diene selected from hexadiene and norbornene derivatives.
8. A composition according to any one of Claims 1 to 7, wherein the component (c) is a rigid polymer having a Vicat softening point of not less than 100°C.
- 30 9. A composition according to any one of Claims 1 to 8, wherein the component (c) is a crystalline polypropylene or a crystalline copolymer of propylene with ethylene in an amount of not more than 10 mol % or a mixture thereof.
- 35 10. A composition according to any one of Claims 1 to 9, wherein the components are in amounts such as to satisfy the expression
- 40 
$$0.87 \leq b/(b+c) \leq 0.40$$
- in terms of weight ratio.
11. A composition according to Claim 1 substantially as described in any one of the Examples.
- 45 12. A composition according to Claim 1 in the form of an unstretched film.